

## DESCRIPTION

PRODUCTION PROCESS FOR FINE CARBON FIBER

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## Technical Field

The present invention relates to a production process for a fine carbon fiber such as a vapor grown carbon fiber and a carbon nanotube, specifically to a technique for continuously and stably producing a fine carbon fiber at a low cost.

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## Background Art

Attentions are paid most to a carbon nanotube among fine carbon fibers. A carbon nanotube is a kind of vapor grown carbon fiber (VGCF) which has so far been researched, and a fine carbon fiber is variously called depending on a size of the fibers. In general, a fiber having a fiber diameter of 1  $\mu\text{m}$  or more is called a vapor grown carbon fiber (VGCF); a fiber having a fiber diameter of 50 nm or less is called a carbon nanotube (CNT); and a fiber having a fiber diameter of larger than 50 nm and smaller than 1  $\mu\text{m}$  which falls in the middle of both of the above fibers is called a carbon nanofiber (CNF).

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A crystal structure of the above fine carbon

materials assumes various forms and includes a single-walled carbon nanotube (SWNT) having a shape in which a single layer of a graphene sheet constituted from carbon is wound into a cylindrical form, a multi-walled carbon nanotube (MWNT) having a structure in which several layers of graphene sheets are laminated like a concentric circle or an annual ring and a nanocone having a crystal structure falling in the middle of the both described above, that is, a conical structure in which crystal planes spread at a constant angle to a central axis thereof.

A fine carbon material having a shape other than a tube includes a ribbon-like fine carbon material having a structure in which graphene sheets are laminated so that they cross orthogonally against a fiber direction and a coil-like fine carbon material having an amorphous structure showing no crystallinity.

All these VGCF, CNF and CNT are fine carbon fibers, and therefore they have so far been produced usually by crystallizing carbon from a gas phase by a thermal decomposition method of hydrocarbon and CO in the presence of transition metal catalyst.

The first step of research in the present field resides in research of a vapor grown carbon fiber in the 1970s. In the development of initial VGCF, the fibers

had a large diameter, and they were produced mainly by a fixed bed method (catalytic chemical vapor deposition method: CCVD method) in which reaction was carried out with a catalyst placed on a substrate or carried on a carrier. However, in an initial fixed bed method having the purpose of producing VGCF having a relatively large fiber diameter, the fiber was grown at a slow speed and produced in a low reaction yield, and therefore it was difficult to industrially put the method to practical use. However, attentions were paid to the point that a very fine fiber having a diameter of 50 nm or less could be produced, and it was industrialized by Hyperion Catalyst International Inc. in U.S. in 1990s.

On the other hand, a CVD (chemical vapor deposition) process in which reaction is carried out while allowing a catalyst to fluidize without using a carrier was developed in 1980s, and the yield was notably improved. In 1990s, industrialization in CNF having a diameter of a level of 100 nm was succeeded (Showa Denko K. K. and Nikkiso Co., Ltd.).

It was reported that a carbon nanotube having the finest fiber diameter could readily be produced by an arc process (Nature, 1991 (354), 56 to 58), and since then, it has actively been tried to develop carbon fibers having a smaller fiber diameter. A production process

for a single-walled carbon nanotube and a multi-walled carbon nanotube each having a fine fiber diameter of 50 nm or less, particularly 10 nm or less has come to be developed mainly by a process in which a fiber is produced by volatilizing carbon at a very high temperature as is the case with an arc process and a laser process and a CCVD process in which a carbon nanotube is formed on a fixed bed prepared by carrying a catalyst on a conventional ceramic carrier.

A carbon nanotube can be used as a filler material for an electron beam source and a composite material which are used for an image display apparatus and a semiconductor production apparatus, and in this case, it is preferred that the carbon nanotube is crystalline and straight and that it has a fine and even fiber diameter. If the carbon nanotube is not straight and curled, the carbon fibers themselves are liable to be entangled to form flocks. If flocks are formed, they are less liable to be crushed, and it becomes difficult to align the carbon fibers in use. Further, when the carbon fibers are added to a resin and the like as a filler material, they are less liable to be evenly dispersed, so that a composite having the desired characteristics is less liable to be obtained.

When an arc process, a laser process or a CVD

process is applied in order to produce a carbon nanotube having the characteristics described above, the following problems used to be involved therein.

In the arc process and the laser process, firstly, the productivity is low since it is difficult to make a production facility thereof large-scale, and it is difficult as well to make a production line continuous. Secondly, in the current arc process, the production efficiency is low since non-fibrous carbon is liable to be produced simultaneously, and it is difficult to separate and collect carbon nanotubes from non-fibrous carbon. Accordingly, it is difficult to produce a carbon nanotube having high quality suited to industrial products by the arc process and the laser process.

On the other hand, the CVD process is the most preferred process for mass production, but it is difficult to make the fiber diameter small in production by the CVD process, and the fiber diameter is liable to be uneven. Further, even if it is possible to make the fiber diameter small by controlling the production conditions, there used to be the problem that a curled carbon nanotube is liable to be produced.

Accordingly, attentions are paid to CCVD in which a carbon nanotube having a fine fiber diameter is produced by using a fixed bed carried thereon with a catalyst.

The production process of a carbon nanotube according to this CCVD process is almost the same as that of a CCVD process which had been investigated in the initial stage of developing VGCF described above, but it is different in that a porous carrier having fine pores such as zeolite is used as the carrier. Use of such specific carrier has made it possible to prepare fine catalyst particles making use of those pores and produce a very fine carbon nanotube (Kingsuk Mukhopadhyay, Akira Koshino, Toshiki Sugai, Nobuo Tanaka, Hisanori Shinohara, Zoltan Konya, B. Nagy; Chemical Physics Letters 303 (1997) 117).

Fig. 5 is a schematic constitutional drawing of a production process for producing a fine carbon fiber by a conventional batch type CCVD process. A production facility 200 shown in this drawing is equipped with a cylindrical reaction furnace 201 placed horizontally, a heater 202 disposed surrounding the periphery of the reaction furnace 201 in order to heat the reaction furnace 201 from the outside, a raw material gas-feeding part 203 and a carrier gas-feeding part 204 which are connected to a right end side of the reaction furnace 201 as shown in the drawing and a supported catalyst-feeding part 205 connected to a left end side of the reaction furnace 201 as shown in the drawing. Further, a first carbon fiber-collecting part 206 for collecting the

supported catalyst which is introduced into the reaction furnace from the supported catalyst-feeding part 205 and used for the reaction together with a fine carbon fiber produced thereon is connected to the right end side of the reaction furnace 201, and a bag filter 208 for receiving a reacted gas from the reaction furnace 201 and separating the reacted gas into the fine carbon fiber and a waste gas is connected to the left end side of the reaction furnace 201.

The bag filter 208 is provided with a gas-discharging part 208a and a solid discharging part 208b. A waste gas-treating apparatus 210 and a second carbon fiber collecting part 209 are connected to the gas-discharging part 208a and the solid discharging part 208b described above respectively, and the waste gas separated by the bag filter 208 is discharged into the waste gas-treating apparatus 210, while the fine carbon fiber which is solid is collected in a second carbon fiber-recovering part 209.

In the production facility for a fine carbon fiber shown in Fig. 5, the supported catalyst such as a catalyst carried on zeolite is introduced from the supported catalyst-feeding part 205 into the reaction furnace 201 charged with a raw material gas and a carried gas, and the fine carbon fiber is allowed to grow on the

supported catalyst by thermal decomposition reaction. The supported catalyst holding the fine carbon fiber on the surface thereof is collected in the first carbon fiber-collecting part 206. Also, the reacted gas after  
5 used for the reaction is discharged into the bag filter 208 from the reaction furnace 201, and it is separated into the fine carbon fiber and the waste gas by the bag filter 208. Then, the fine carbon fiber separated by the bag filter 208 is collected into the second carbon fiber-  
10 collecting part 209, and the waste gas is sent to the waste gas-treating apparatus 210. Thus, the fine carbon fiber can be produced by the CCVD process using the production facility shown in Fig. 5.

On the other hand, a large amount of a carrier gas  
15 (hydrogen, inert gas and the like) has to be introduced into a reaction furnace in producing a vapor grown carbon fiber and a carbon nanotube by the CCVD process and the CVD process described above, and therefore it is a large factor by which the production cost grows high.

20 Further, in the production by the CCVD process and the CVD process described above, the unreacted raw material gas, low boiling components and high boiling components which are by-products are contained in the reacted gas after used for the reaction, and therefore  
25 they can not be discharged to the outside as they are in



order to prevent the environment from being polluted. Accordingly, waste gas treatment such as, for example, incineration treatment and adsorption treatment is required for discharging the above gas to the outside.

5 Since a large amount of a carrier gas is used, as described above, in the production by the CCVD process and the CVD process, an amount of the waste gas itself is increased, and a cost for waste gas treatment grows large.

10 Further, sulfide such as hydrogen sulfide and thiophene are added in a certain case for the purpose of accelerating reaction of producing a carbon fiber. In this case, a sulfur compound is contained in the waste gas, and therefore it has to be removed. However, an amount of the waste gas itself is large as described  
15 above, so that the treating cost is increased very much.

As described above, the production cost can not help growing high in the CCVD process and the CVD process because of the large amounts of the gas used and the waste gas amount, and it used to be a large problem in  
20 mass-producing a fine carbon fiber.

An object of the present invention is to provide a production process in which a fine carbon fiber such as a vapor grown carbon fiber and a carbon nanotube each having an optional fiber diameter, particularly a fine  
25 fiber diameter can continuously and stably be produced at

a low cost.

#### Disclosure of the Invention

5 Earnest investigations repeated by the present inventors in order to solve the problems described above have resulted in finding that in a process for producing a fine carbon fiber by a thermal decomposition process (CVD process and CCVD process) of CO and an organic compound using ultra fine particles comprising a transition metal as a catalyst, use of at least one organic compound containing a VIB group element in the periodic table of elements in a molecule as a raw material makes it possible to produce a fine carbon fiber having high quality and a very fine fiber diameter and that use of the above organic compound for the raw material makes it possible to readily separate and recover reaction by-products and the unreacted raw material from the reacted gas and recycling of the reacted gas into a reaction furnace makes it possible to reduce the amounts of a carrier gas and a waste gas.

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The production process for a fine carbon fiber according to the present invention comprises introducing a raw material gas comprising an organic compound, a carrier gas comprising hydrogen and/or an inert gas and a catalyst comprising ultra fine particles containing at

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least one transition metal into a reaction furnace to produce a fine carbon fiber in the reaction furnace described above by thermal decomposition reaction, wherein an organic compound containing a VIB group element in the periodic table of elements in a molecule is used as the raw material organic compound, and the reaction is carried out at a pressure of  $2 \times 10^5$  Pa or less. After collecting the fine carbon fiber from a reacted gas used for producing the fine carbon fiber, the reacted gas is further cooled, and the fine carbon fiber is collected by a different separating and collecting apparatus having higher separating ability. Then, at least a part of the above reacted gas, preferably gas obtained by removing by-products and unreacted gas from the reacted gas is reintroduced into the reaction furnace by a recycling means connected to the reaction furnace described above and used.

Not only the fine carbon fiber is produced in the reaction furnace, but also low boiling components, high boiling components and hydrogen gas are produced as by-products by decomposition reaction, and they are contained in the gas coming out from the reaction furnace together with the unreacted raw material gas and the carrier gas. If the above by-products are stuck onto the inner wall of the production facility, pipelines and

equipments constituting the production facility are likely to be clogged.

In the present invention, an organic compound containing a VIB group element in the periodic table in a molecule is used as the raw material. The VIB group element is preferably oxygen and sulfur, particularly oxygen. For example, when a compound containing oxygen is used, water, CO, CO<sub>2</sub> and hydrogen are produced as by-products.

In reference to the organic compound containing a VIB group element in a molecule, the compound containing oxygen includes alcohols, ketones, phenols, ethers, aldehydes, organic acids and esters.

To be specific, it includes, for example, methanol, ethanol, propanol, cyclohexanol, acetone, methyl ethyl ketone, acetophenone, cyclohexanone, phenol, cresol, formaldehyde, acetaldehyde, formic acid, acetic acid, propionic acid, oxalic acid, succinic acid, adipic acid, dimethyl ether, diethyl ether, dioxane, methyl acetate and ethyl acetate.

The sulfur compound includes thiols, thioethers and thiophenes, and thioethers can particularly be used.

The above raw material organic compounds can be fed into the reaction furnace by spraying in the form of gas, liquid, solution or solid.

The above compounds can be used alone or in a mixture of two or more kinds thereof.

The fine carbon fiber of the present invention is produced by the CVD process or the CCVD process, and  
5 ultra fine particles comprising a transition metal are used as the catalyst.

The transition metal includes, for example, iron, cobalt, nickel, yttrium, titanium, vanadium, manganese, chromium, copper, niobium, molybdenum, palladium,  
10 tungsten and platinum. In addition to the metals of simple substances, the compounds thereof can be used as the catalyst. Further, they may be used alone or in combination of two or more kinds selected from them. The larger catalytic effect is obtained depending on the  
15 combination.

In respect to the form of the compounds, the organic compounds, the inorganic compound or the combination thereof can be used. For example, ferrocene, nickelocene and cobaltocene can be used as the organic  
20 compounds. Also, the inorganic compounds may assume any form of oxide, nitrate, sulfate and chloride.

Further, in order to raise an efficiency of fiberization, a sulfur compound such as sulfur,  $H_2S$ ,  $CS_2$ ,  $SO_2$  and thiophene may be added when putting the raw  
25 material and the catalyst into the reaction furnace.

When using such compound, the same effect can be obtained even if the raw material organic compound is an organic compound containing no VIB group element in a molecule such as hydrocarbons.

5           The catalyst may be fine particles themselves of the metals or the compound described above (CVD process), and the metals or the compounds described above may be carried on fine particles of an inorganic carrier (CCVD process). For example, alumina, zeolite, carbon,  
10           magnesia and calcia can be used as the inorganic carrier.

          An introducing method of the catalyst may be any of a method of gasifying alone, a method of gasifying after mixed with the raw material carbon source, a method of diluting with a carrier gas and a method of dissolving in  
15           the raw material carbon source and feeding in a liquid form.

          In the present invention, carbon having no crystallinity and the VIB group element participate in the reaction by using the catalyst comprising a  
20           transition metal and using the organic compound containing a VIB group element in a molecule as the raw material, whereby capable of being obtained are single-walled and multi-walled carbon nanotubes in which a purity is high and a fiber diameter is as fine as 10 nm  
25           or less and which has an axial chiral structure.

According to the production process for the fine carbon fiber of the present invention, the reacted gas used for producing the fine carbon fiber is introduced again into the reaction furnace by a recycling means, whereby the reacted gas which has so far been entirely discharged to the outside can effectively be used. This makes it possible to reduce a use amount of the carrier gas as well as an amount of the waste gas, and therefore both of a cost for the carrier gas and a cost for treating the waste gas can be reduced. Accordingly, it becomes possible to reduce a cost relating to the production of the fine carbon fiber as compared with those of conventional ones. In particular, a concentration of the raw material gas in the reaction furnace has to be maintained dilute in order to produce a carbon nanotube having a fine fiber diameter of 10 nm or less. That is, an amount of the carrier gas is increased, and a concentration of the raw material is diluted. In such sense, it is effective to recycle the reacted gas.

The production process for the fine carbon fiber of the present invention is a process for producing a fine carbon fiber by a thermal decomposition method using the VIB group element-containing organic compound as the raw material and using ultra fine particles comprising a transition metal as the catalyst, and the production

process comprises a reaction furnace for allowing thermal decomposition reaction in an inside thereof to proceed to produce a fine carbon fiber, a raw material gas-feeding part for feeding a raw material gas into the reaction furnace, a carrier gas-feeding part for feeding a carrier gas into the reaction furnace, a carbon fiber-separating apparatus for separating and collecting the fine carbon fiber produced in the reaction furnace from a reacted gas, a recycling means for cooling the reacted gas to introduce it again into the reaction furnace and preferably an apparatus for condensing and separating condensing components contained in the above reacted gas.

In the production of the fine carbon fiber of the present invention, the separating apparatus described above is connected to the carbon fiber-collecting apparatus; the fine carbon fiber separated from the reacted gas by the separating apparatus is collected in the carbon fiber-collecting apparatus; the reacted gas coming out from the separating apparatus is cooled, and then the cooled gas is allowed to pass through another separating apparatus to further collect the fine carbon fiber. The gas coming out from the carbon fiber-collecting apparatus can be directly discharged after waste gas treatment. In the process of the present invention, however, the gas remaining after collecting



the fine carbon fiber is recycled to the reaction furnace by the recycling means described above. In this case, the above gas is further cooled to condense condensing components such as water produced by the reaction and the unreacted raw material, and then the gas is introduced into the reaction furnace after separating them. On the other hand, the condensate separated is subjected to waste liquid treatment and then discharged. Further, the unreacted raw material can be separated from the condensate and recycled as the raw material.

Further, the unreacted raw material, produced water and high boiling by-products are stuck in a certain case on the fine carbon fiber which is the product obtained from the separating and collecting apparatus, and therefore the product is once heated to vaporize them, whereby the product having a higher purity can be obtained. The raw material compound can be separated from the vaporized components and recycled as the raw material.

The raw material compound can be separated from the condensate and the vaporized components each described above by one method of distillation, adsorption and membrane separation or a method in which two or more of them are combined.

If assuming such constitution, a collecting rate of

the fine carbon fiber to a charged amount of the raw material can be enhanced by collecting the fine carbon fiber as well from the reacted gas cooled after separating the fine carbon fiber from the reacted gas, and an increase in the production cost brought about by reduction in the collecting rate can be prevented.

The fine carbon fiber produced by thermal decomposition reaction has a very small bulk density and is light, so that the total amount thereof or the carbon fiber peeled from the catalyst floats in the reaction furnace. Accordingly, the reacted gas discharged from the reaction furnace is accompanied with the fine carbon fibers and the reaction by-products. If gas used for recycling is reintroduced into the reaction furnace as it is mixed with the fine carbon fiber and subjected to the reaction, carbon grows further on the fine carbon fibers to enlarge a fiber diameter (broaden a width of a fiber diameter), so that the desired fiber diameter is not likely to be obtained. Accordingly, the fine carbon fiber contained in the reacted gas is removed in the present invention by providing the separating means described above so that only the gas component is reintroduced into the reaction furnace, whereby the fiber diameter is prevented from becoming large. This makes it possible to stably produce the fine carbon fiber having a

desired fiber diameter.

Also, if solids such as the fine carbon fiber and high boiling by-products contained in the reacted gas are circulated in the insides of the reaction furnace and the recycling means, they are likely to be stuck on the insides of pipes connecting them to clog the pipes. According to the constitution described above, however, the solids such as the fine carbon fiber and the condensate are separated by the separating apparatus, and the gas reintroduced into the reaction furnace does not contain the solids and the condensate. Accordingly, such trouble as described above can be prevented beforehand, and it becomes possible to stably produce the fine carbon fiber.

In the production process for the fine carbon fiber of the present invention, a filter, a cyclone and a device obtained by combining them each of which has a function to efficiently separate solids from gas are suitably used as a separating means. The most suited one can be selected from the above filter and cyclone according to an amount and a temperature of the gas.

For example, when an amount of the reacted gas is large, an amount of the fine carbon fiber collected in the separating means becomes large as well, and therefore a load charged on one filter has to be controlled so that

it does not become so large. In this case, combination of a filter having a large mesh and a bag filter having a fine mesh or combination of a filter and a cyclone are recommendable.

5           The gas coming out from the reaction furnace stays, though depending on a temperature of the reaction furnace, in a high temperature of about 600°C or higher. When using a bag filter, the gas of such a high temperature can not be allowed to pass through it, and therefore  
10 separation by the bag filter described above is preferably carried out after the temperature of the reacted gas is lowered. To be specific, a cooling means such as a water-cooled jacket is provided in a path from the reaction furnace or the carbon fiber-collecting part  
15 to the separating apparatus to cool the reacted gas. The gas is cooled down to 40°C or higher to 150°C or lower (preferably 100°C or lower) by the above cooling means, and then separation by the bag filter is carried out. A solid product which is less liable to be cooled is mixed  
20 in the reacted gas in a certain case, and therefore it is advisable to use a bag filter which can endure as high temperature as possible for the filter.

          In the production process for the fine carbon fiber of the present invention, the gas obtained after  
25 separating the fine carbon fiber is further cooled to

recover the unreacted raw material organic compound and the condensate such as produced water, and they can be separated by an apparatus in which two or more methods of distillation, adsorption and membrane separation are combined.

Next, in the production process for the fine carbon fiber of the present invention, when recycling the reacted gas, a temperature of the gas reintroduced into the reaction furnace is preferably controlled to 40°C or higher.

Substances produced in the reaction furnace are not restricted only to the fine carbon fiber, and the unreacted hydrocarbon and the organic compounds of low boiling components and high boiling components are contained as by-products in the reacted gas discharged from the reaction furnace. If the organic compounds are stuck on the inner wall of the production facility, they are likely to clog pipelines constituting the production facility. A measure for preventing these pipelines from being clogged is required in order to safely carry out the production. Various investigations on production conditions therefor repeated by the present inventors have resulted in finding that if a temperature of the gas which passes through at least the recycling means described above and is reintroduced into the reaction

furnace is controlled to 40°C or higher, the organic compounds are almost completely prevented from being deposited and that as a result, the pipelines can be prevented from being clogged. That is, organic compounds  
5 can be controlled so that they are not deposited from the raw material gas, the reacted gas and the recycled gas in the facility by controlling a temperature of the gas when passing through the recycling means in which the temperature of the gas becomes the lowest in the whole of  
10 the production facility to 40°C or higher. Accordingly, when the temperature of the gas is lower than 40°C in a position where the temperature of the gas becomes the lowest, the gas is, if necessary, thermally insulated by a means such as covering or heated so that it is  
15 maintained at 40°C or higher.

Also, the temperature of the gas which passes through the inside of the recycling means described above and is reintroduced into the reaction furnace is more preferably 60°C or higher. That is, if the temperature  
20 of the gas is 60°C or higher, the organic compounds can more effectively be inhibited from being deposited from the gas, and therefore further stable production shall be possible.

In respect to a position where the reaction gas  
25 described above is reintroduced into the reaction furnace,

it may be returned directly to the reaction furnace or may be mixed with the raw material gas and/or the carrier gas and then reintroduced into the reaction furnace. In the case of the latter, for example, in the case where a liquid raw material is gasified for use, the reacted gas is preferably heated to a prescribed temperature in advance so that the raw material gas and the reacted gas mixed are not liquefied.

Next, in the production process for the fine carbon fiber of the present invention, 20 % or more of the reacted gas described above is preferably reintroduced into the reaction furnace by the recycling means and used. Assuming the above constitution makes it possible to obtain a marked cost-reducing effect by reduction in an amount of the carrier gas and an amount of the waste gas. It is more preferably controlled to 50 % or more, but if an organic compound is used for the raw material gas, hydrogen is produced by thermal decomposition reaction, so that an amount of hydrogen contained in the gas coming out from the reaction furnace grows larger than an amount of hydrogen introduced as the carrier gas. Accordingly, the increment of hydrogen due to gas generation has to be discharged. That is, an amount of the gas reintroduced into the reaction furnace for recycling is up to the same amount at the most as that of the carrier gas to be

introduced into the reaction furnace.

In the production process for the fine carbon fiber of the present invention, the inside of the recycling means described above is preferably a positive pressure to an atmospheric pressure.

In the production process for the fine carbon fiber of the present invention, when reusing the reacted gas by circulating, the reacted gas contains surely hydrogen gas and the raw material organic compound. If oxygen is mixed in the hydrogen gas and the organic compound, a fire and large explosion are likely to be brought about. In order to prevent them, the inside of the system in the facility including the pipelines has to be maintained at a positive pressure without being a negative pressure. In particular, a suction side of the gas circulating means for circulating the gas in the facility is most liable to be a negative pressure, and therefore a measure is preferably undertaken so that this part does not become a negative pressure.

To be specific, the following can be given as the measure for preventing a negative pressure:

- (1) increasing a diameter of a pipeline at a suction side of the gas circulating means described above as much as possible,
- (2) operating while monitoring a pressure of a suction



side of the gas circulating means described above,

(3) controlling so that the facility can be stopped when the pressure becomes a negative pressure,

5 (4) controlling so that a safety gas (for example, inert gas such as  $N_2$ , Ar and the like) can be introduced into the facility when the pressure becomes a negative pressure and

10 (5) constituting the system having a circulating system for controlling pressure before and after the gas circulating means.

In the production of the fine carbon fiber of the present invention, a raw material gas fed from a raw material gas-feeding source and a carrier gas fed from a carrier gas-feeding source may be fed separately to the  
15 reaction furnace, or may be fed in a mixture of a reaction gas. In the case of the latter, the raw material and the carrier gas are mixed to produce the reaction gas, and the reaction gas is introduced into the reaction furnace.

20 Also, when the reacted gas is recycled, the recycle gas is preferably mixed with the carrier gas and introduced into the reaction furnace.

For example, when an organic compound which is liable to be liquefied is used for the raw material gas,  
25 the raw material gas can be prevented from being

liquefied by assuming the above constitution, and therefore clogging of the pipelines and an instability in the raw material concentration can be prevented. Accordingly, the facility can stably be operated, and this makes it possible to enhance homogeneity of the fine carbon fiber produced.

Further, an amount of the carrier gas which is newly charged can be reduced, and an amount of the waste gas can be reduced as well, so that both of a carrier gas cost and a waste gas treatment cost can be reduced. Accordingly, the fine carbon fiber can readily be produced at a low cost by means of the CVD process and the CCVD process by using the production facility for the fine carbon fiber of the present invention.

#### Brief Description of the Drawings

Fig. 1 is a constitutional drawing schematically showing the production process for the embodiment of the reference example.

Fig. 2 is a constitutional drawing schematically showing the production process for the first embodiment.

Fig. 3 is a constitutional drawing schematically showing the production process for the second embodiment.

Fig. 4 is a constitutional drawing schematically showing the production process for the third embodiment.

Fig. 5 is a constitutional drawing schematically showing the production process by a conventional batch type CCVD process.

5                   Best Mode for Carrying out the Invention

The embodiments of the present invention shall be explained below with reference to the drawings.

Embodiment of the reference example

10           Fig. 1 is a constitutional drawing schematically showing the production process for the fine carbon fiber showing the embodiment of the reference example which is the base of the present invention. The production process of the present invention shown in the above  
15 drawing is a production process for producing a fine carbon fiber by the CCVD process, and it is constituted from a cylindrical reaction furnace 3, a raw material gas-feeding part 2, a carrier gas-feeding part 1 and a catalyst-charging apparatus 20 which are connected to an  
20 inlet side end of the reaction furnace, a fine carbon fiber-separating and collecting apparatus 4 connected to an outlet side end of the reaction furnace 3, a fine carbon fiber-collecting tank 8 connected to a lower part of the fine carbon fiber-separating and collecting  
25 apparatus 4, a reacted gas-cooling apparatus 6 connected

to an upper part of the same, a second fine carbon fiber-separating and collecting apparatus 5 for further separating the fine carbon fiber from a cooled gas and a waste gas-treating apparatus 12.

5           When producing the fine carbon fiber by the production process shown in Fig. 1, the reaction furnace 3 is first heated and maintained at 600°C or higher to 1250°C or lower by a heater equipped to the reaction furnace 3. The foregoing temperature of the reaction  
10           furnace shows one example of the production conditions, and actually, it is set to the optimum condition depending on combination of the kind of a carbon source (an oxygen-containing organic compound and the like) which is used as a raw material, the kind of a catalyst  
15           and the kind of a carrier gas.

          Next, a raw material gas comprising an organic compound containing a VIB group element in a molecule is introduced as a carbon source for a fine carbon fiber into the reaction furnace 3 from the raw material-feeding  
20           part 2, and a carrier gas comprising hydrogen, methane or an inert gas is introduced into the reaction furnace 3 from the carrier gas-feeding part 1. Further, a catalyst for causing the reaction of fiberizing carbon in the reaction furnace 3 is introduced into the reaction  
25           furnace 3 together with the above gases. Then, the raw

material gas is decomposed with heat in the reaction furnace 3, and a fine carbon fiber is produced by the action of the catalyst.

5       Next, the fine carbon fiber produced is sent to the fine carbon fiber-separating and collecting apparatus 4 together with the gas in the reaction furnace. Then, the fine carbon fiber is separated from a reacted gas by the fine carbon fiber-separating and collecting apparatus 4 and sent to the fine carbon fiber tank 8. The gas coming  
10       out from the fine carbon fiber-separating and collecting apparatus 4 is cooled to 40°C or higher to 150°C or lower and comes into the second fine carbon fiber-separating and collecting apparatus 5, wherein the fine carbon fiber is further collected by a separating device which can be  
15       used for a low temperature gas, such as a bag filter, to be stored in the collecting tank 8. On the other hand, the gas coming out from the second fine carbon fiber-separating and collecting apparatus 5 is discharged to the outside of the system after treated by the waste gas-  
20       treating apparatus.

#### First embodiment:

Next, the first embodiment of the present invention shall be explained with reference to Fig. 2.

25       The same elements as the constitutional elements

shown in Fig. 1 among constitutional elements shown in Fig. 2 shall be represented with the same symbols, and detailed explanations therefor shall be omitted (the same shall apply to the following embodiments).

5            Fig. 2 is a constitutional drawing schematically showing the production process for the fine carbon fiber which is the first embodiment of the present invention. The production process of the present invention shown in the above drawing is a production process for producing a  
10   fine carbon fiber by the CCVD process, and it is a process equipped with a recycling apparatus. That is, in the embodiment of the reference example described above, the gas coming out from the second fine carbon fiber-separating and collecting apparatus 5 is discharged to  
15   the outside of the system after treated by the waste gas-treating apparatus. However, this is a process in which a part thereof is circulated to the reaction furnace by a gas-circulating blower 9. In this process, a circulated gas and a discharged gas can freely be controlled, and  
20   therefore a gas-circulating amount in the reaction system can readily be controlled.

          This makes it possible to reduce an amount of a carrier gas made up, and as a result to reduce an amount of a waste gas. Further, the unreacted raw material gas,  
25   the VI group element-containing compound and the by-

products can be returned to the reaction system, and therefore the yield can be increased.

Further, the fine carbon fiber is separated at two stages by the separating apparatus 4 and 5, and therefore the fine carbon fiber is not mixed in the circulated gas, so that the fiber can be prevented from becoming thick by allowing carbon to further grow on the fiber.

Second embodiment:

Fig. 3 is a constitutional drawing schematically showing the production process for the fine carbon fiber which is the second embodiment of the present invention. The production process of the present invention shown in the above drawing is a production process in which in the first embodiment described above, a part of the gas coming out from the second fine carbon fiber-separating and collecting apparatus 5 is further cooled by another cooling apparatus 7 which is different from the cooling apparatus 6 before the gas is circulated to the reaction furnace by the gas-circulating blower 9, so that reaction by-products such as water and the non-decomposed raw material organic compound which are contained in the gas are condensed and then separated and removed from the gas to circulate the gas. The condensate separated is sent to a moisture separator 11 via a condensate tank 10 to

recover the condensate such as water and an organic compound gas, and this gas is circulated as well to the reaction furnace 3. The condensate stored in the moisture separator 11 is discharged to the outside of the system after treated by a waste water-treating apparatus 15.

In the above process, water and organic compounds having a relatively high boiling point are not contained in the circulated gas, and therefore the moisture concentration is controlled to a lower level. Accordingly, the moisture can be inhibited from being condensed, and the pipelines can be prevented from being clogged.

#### Third embodiment:

Fig. 4 is a constitutional drawing schematically showing the production process for the fine carbon fiber which is the third embodiment of the present invention. The second embodiment described above is a process in which only the gas circulated to the reaction furnace by the gas-circulating blower 9 out of the gas coming out from the second fine carbon fiber-separating and collecting apparatus 5 is cooled by the cooling apparatus 7 to further lower a temperature of the gas, so that the reaction by-products contained in the gas such as water



and the non-decomposed raw material organic compound are condensed and then separated and removed from the gas to circulate the gas. However, the production process of the present invention shown in the above drawing is a production process in which the total amount of the gas coming out from the second fine carbon fiber-separating and collecting apparatus 5 is cooled by the cooling apparatus 7 to separate condensate contained in the above gas. A part of the gas remaining after separating the condensate is circulated to the reaction furnace by the blower 9, and the residual gas is sent to a waste gas-treating apparatus 12 and discharged to the outside of the system after treated. On the other hand, the condensate separated is sent to a moisture separator 11 via a condensate tank 10 to recover the condensate such as water and the organic compound, and this gas is circulated as well to the reaction furnace 3. The condensate stored in the gas-liquid separator 11 is discharged to the outside of the system after treated by a waste water-treating apparatus 15.

In this process, not only the total amount of the effective organic compound is recycled, but also water and organic compounds having a relatively high boiling point are not contained in the circulated gas, and therefore a moisture concentration in the system is

controlled to a lower level. Accordingly, the moisture is inhibited from being condensed, and the pipelines are prevented from being clogged. Further, components to be condensed are not entered into the waste gas-treating apparatus, and therefore a load charged thereon is reduced.

### Examples

The present invention shall be explained below in further details with reference to examples and a reference example, but the present invention shall by no means be restricted to the examples described below.

### Reference Example

Carried out by the process shown in Fig. 1. A reaction furnace used is of a structure in which an SiC-made reaction tube having an inner diameter of 200  $\phi$  is heated from the outside, and it is a reaction furnace of a rotary type in which the reaction tube can be rotated at a constant speed. Ethyl alcohol was used for a raw material of the carbon source and continuously charged at a flow rate of 7.4 NL/minute. Argon was used for a carrier gas, and a flow rate thereof was set to 5 NL/minute. A catalyst prepared by carrying two components of molybdenum and cobalt on magnesium oxide

having an average particle diameter of 0.1  $\mu\text{m}$  or less according to a conventional method and then activating it in an inert gas was charged at a rate of 15 g/min. The reaction temperature was set to 810°C, and the reaction pressure was set to an atmospheric pressure to continuously carry out the reaction at a rotating speed of 3 rpm.

As a result of the reaction, obtained was 19 g/min of crude CNT which includes the catalyst and volatile components and is collected in a CNT-collecting tank. A CNT content in the crude CNT was 3.8 g/min.

#### Example 1

The present example was carried out by the process shown in Fig. 2. Used for a reaction furnace was a reaction tube of a rotary type having a structure in which the same SiC-made reaction tube having an inner diameter of 200  $\phi$  as in the reference example was heated from the outside and in which the reaction tube could be rotated at a constant speed. Ethyl alcohol was used for a raw material of the carbon source as was the case with the reference example, and it was continuously charged at a flow rate of 7.4 NL/minute. A molybdenum and cobalt base catalyst carried on magnesium oxide having an average particle diameter of 0.1  $\mu\text{m}$  or less was activated

in an inert gas and then charged at a rate of 15 g/min. The reaction temperature was set to 805°C, and the reaction pressure was set to an atmospheric pressure to continuously carry out the reaction at a rotating speed of 2 rpm. Recycled was the reacted gas (containing unreacted ethyl alcohol and decomposition products) corresponding to 20 % of argon gas contained in the reacted gas at the outlet, and the remained gas was sent to a waste gas-treating system. Accordingly, the carrier gas in the furnace was argon gas and was controlled so that a newly charged argon gas was 4 NL/min.

As a result of the reaction, the catalyst and crude CNT which were collected in a CNT-collecting tank were 19.3 g/min, and a CNT content in the crude CNT was 4.0 g/min. The CNT yield was more improved by 0.2 g/min than the case where recycling was not carried out, and an amount of argon charged was reduced by 20 %.

#### Example 2

The present example was carried out by the process shown in Fig. 3. Used for a reaction furnace in the present example was a reaction tube of a rotary type having a structure in which an SiC-made reaction tube having an inner diameter of 200  $\phi$  was heated from the outside and in which the reaction tube could be rotated

at a constant speed. Ethyl alcohol was used for a raw material of the carbon source as was the case with the reference example, and it was continuously charged at a flow rate of 7.4 NL/minute. A molybdenum and cobalt base catalyst carried on magnesium oxide having an average particle diameter of 0.1  $\mu\text{m}$  or less was activated in an inert gas and then charged at a rate of 15 g/min. The reaction temperature was set to 815°C, and the reaction pressure was set to an atmospheric pressure to continuously carry out the reaction at a rotating speed of 1 rpm. The reacted gas corresponding to 50 % of argon gas contained in the reacted gas at the outlet was recycled to the reaction system after cooled by a cooler 7 to remove water by a moisture separator. Then, the remained gas was sent to a waste gas-treating system. The carrier gas in the furnace comprised 3 NL/min as a newly charged portion and 3 NL/min as a recycled portion.

As a result of the reaction, the catalyst and crude CNT which were collected in a CNT-collecting tank were 19.6 g/min, and a CNT content in the crude CNT was 4.2 g/min. The CNT yield was more improved by 0.4 g/min than the case where recycling was not carried out, and an amount of argon charged was reduced by 50 %.

### Example 3

The present example was carried out by the process shown in Fig. 4. Used for a reaction furnace in the present example was a reaction tube of a rotary type having a structure in which an SiC-made reaction tube having an inner diameter of 200  $\phi$  was heated from the outside and in which the reaction tube could be rotated at a constant speed. Ethyl alcohol was used for a raw material of the carbon source as was the case with the reference example, and it was continuously charged at a flow rate of 7.4 NL/minute. A molybdenum and cobalt base catalyst carried on magnesium oxide having an average particle diameter of 0.1  $\mu\text{m}$  or less was activated in an inert gas and then charged at a rate of 15 g/min. The reaction temperature was set to 800°C, and the reaction pressure was set to an atmospheric pressure to continuously carry out the reaction at a rotating speed of 1 rpm. The total amount of the reacted gas was cooled in a cooler 7 to recover unreacted components and oxygen-containing hydrocarbons and then recycled to the reaction system after moisture was removed by a moisture separator 11. The reacted gas corresponding to 50 % of argon gas contained in the reacted gas at the outlet of a cooler 7 was recycled, and the remained gas was sent to a waste gas-treating system. The carrier gas in the furnace comprised 3 NL/min as a newly charged portion and 3

NL/min as a recycled portion.

As a result of the reaction, the catalyst and crude CNT which were collected in a CNT-collecting tank were 19.6 g/min, and a CNT content in the crude CNT was 4.7 g/min. The CNT yield was more improved by 0.7 g/min than the case where recycling was not carried out, and an amount of argon charged was reduced by 50 %.

#### Industrial Applicability

The present invention is a process in which a fine carbon fiber can continuously and stably be produced at a high yield and a low cost, and it is suited for producing a carbon nanotube having high quality.